PTO 07-2760 Japanese Patent

10280103

STEEL FOR SOLID ELECTROLYTE TYPE FUEL CELL SEPARATOR

[Kotai Denkaishitsu Kei Nenryo Denchi Separeta Yo Hagane]

Takehiro Ono

UNITED STATES PATENT AND TRADEMARK OFFICE

Washington, D.C. March 2007

Translated by: Schreiber Translations, Inc.

Country	:	Japan
Document No.	:	Hei 10-280103
Document Type	:	Kokai
Language	:	Japanese
Inventor	:	Takehiro Ono
Applicant	:	Hitachi Metals, Ltd.
IPC	:	C 22 C 38/00, 38/18
Application Date	:	April 8, 1997
Publication Date	:	October 20, 1998
Foreign Language Title	:	Kotai Denkaishitsu Kei Nenryo Denchi Separeta Yo Hagane
English Title	:	STEEL FOR SOLID ELECTROLYTE TYPE FUEL CELL SEPARATOR

/1[1]

Specification

1. Title of the invention

Steel for Solid Electrolyte Type Fuel Cell Separator

2. Claims

/2

1. A steel for a solid electrolyte type fuel cell separator, characterized by being comprised of 0.2% or less C, 3.0% or less Si, 1.0% or less Mn, 15-30% Cr, 0.5% or less Hf, and the balance substantial Fe by weight %.

2. A steel for a solid electrolyte type fuel cell separator, characterized by being comprised of 0.2% or less C, 3.0% or less Si, 1.0% or less Mn, 15-30% Cr, 0.5% or less Hf, one kind or two kinds or more of 2% or less Ni, 1% or less Al, 1% or less Ti, 5% or less Mo + 1/2W of one kind or two kinds of Mo and W, and 2% or less Nb, and the balance substantial Fe by weight %.

[1] Numbers in the margin indicate pagination in the foreign text.

3. A steel for a solid electrolyte type fuel cell separator, characterized by being comprised of 0.2% or less C, 3.0% or less Si, 1.0% or less Mn, 15-30% Cr, 0.5% or less Hf, one kind or two kinds or more of 0.5% or less Y, 0.2% or less rare-earth elements, and 1% or less Zr, and the balance substantial Fe by weight %.

4. A steel for a solid electrolyte type fuel cell separator, characterized by being comprised of 0.2% or less C, 3.0% or less Si, 1.0% or less Mn, 15-30% Cr, 0.5% or less Hf, one kind or two kinds or more of 2% or less Ni, 1% or less Al, 1% or less Ti, 5% or less Mo + 1/2W of one kind or two kinds of Mo and W, and 2% or less Nb, one kind or two kinds or more of 0.5% or less Y, 0.2% or less rare-earth elements, and 1% or less Zr, and the balance substantial Fe by weight %.

5. A steel for a solid electrolyte type fuel cell separator, characterized by being comprised of 0.08% or less C, 0.2-2.0% Si, 0.2-1.0% Mn, 18-25% Cr, 0.01-0.3% Hf, 0.9% or less Ni, 0.5% or less Al, one kind or two kinds or more of 0.01-0.3% Y, 0.01-0.12% rare-earth elements, and 0.05-0.8% or less Zr, and the balance substantial Fe by weight %.

3. <u>Detailed explanation of the invention</u>

[0001]

(Technical field of the invention)

The present invention pertains to a steel being used in a separator of a solid electrolyte type fuel cell.

[0002]

(Prior art)

Since a fuel cell has excellent characteristics such as high power generation efficiency, a small amount of SOx, NOx, and CO_2 being generated, good responsivity to the change of a load, and compactness, the application to wide power generation systems such as large-scale centralization type, city suburb distribution type, and self-power generation as substitutes for a steam power generation is expected.

[0003] The kind of fuel cell is classified into phosphoric acid type, molten carbonate type, solid electrolyte type, and high-molecular solid electrolyte type, and among them, the solid electrolyte type fuel cell is operated at about 1,000oC by using a ceramic such as stabilized zirconia as an electrolyte, does not need to use a catalyst in an electrode reaction, can enhance the inside of a fossil fuel at high temperature, can use various fuels such as coal gas, can generate a power with high efficiency by the combination of a gas turbine or steam turbine using a high-temperature heat discharge, so-called a combined cycle power generation, and is compact since all the

constitutional substances are solid. This fuel cell is considered very promising as the next-generation power supply source.

[0004] However, many problems to be reviewed remain for the practicality of the solid electrolyte type fuel cell. Especially in a tabular fuel cell in which a high output density is possible, a separator is mentioned as an important constitutional element. The separator has a role of supporting three layers of an electrolyte, a fuel electrode and an air electrode, forming a gas flow passage, and sending a current. Therefore, it is necessary for the separator to have high-temperature electric conductivity, oxidation resistance, and small thermal expansion coefficient from an electrolyte.

[0005] In consideration of these required characteristics, an electroconductive ceramic has frequently been used. However, since the ceramic has poor workability and is expensive, problems remain in terms of large scale of the fuel cell and practicality. For this reason, the development of a separator made of a metallic material with reliability at low cost is in demand. Also, if an ordinary metallic material is used in the vicinity of 1,000°C, the surface is oxidized, so that an oxide film is generated. Therefore, in order to use it as a separator material, it is necessary for the oxide film to be stably

oxidized, and it is further necessary for the oxide film to have electric conductivity.

[0006] In Japanese Kokai Patent Application No. Hei 6[1994]-264193, as a metallic material for the solid electrolyte type fuel cell, an austenite system stainless steel comprised of 0.1% or less C, 0.5-3.0% Si, 3.0% or less Mn, 15-30% Cr, 20-60% Ni, 2.5-5.5% Al, and the balance substantial Fe is presented. In Japanese Kokai Patent Application No. Hei 7[1995]-166031, it is presented that a material comprised of 60-82% Fe, 18-40% Cr, and additive elements (La, Y, Ce, or Al) for reducing the contact resistance between the separator and an air electrode of the above-mentioned fuel cell is used as a separator of the solid electrolyte type fuel cell. Furthermore, in Japanese Kokai Patent Application No. Hei 7[1995]-145454, a material composed of 5-30% Cr, 3-45% Co, 1% or less La, and the balance substantial Fe is presented as a metallic material for the solid electrolyte type fuel cell.

[0007]

(Problems to be solved by the invention)

Since the material presented in the above-mentioned Japanese Kokai Patent Application No. Hei 6[1994]-264193 includes a considerable amount of Al and Cl, the surface oxide film is mainly composed of an Al system oxide, and a Cr system

oxide is included in it. However, as will be mentioned later, since the Al system oxide has low electric conductivity, this material is not sufficient for a solid electrolyte separator. Furthermore, in the austenite system stainless steel, since the thermal expansion coefficient is large, compared with the zirconia for stabilizing the electrolyte, there is/3 a problem in the stability in a long-time usage. Also, since a large amount of expensive Ni is included, the cost is high, and the practicality of the fuel cell is insufficient.

[0008] In the material presented in Japanese Kokai Patent Application No. Hei 7[1995]-166031 or Japanese Kokai Patent Application No. Hei 7[1995]-145454, compared with the austenite system stainless steel, since the thermal expansion coefficient is low and close to the thermal expansion coefficient of the zirconia for stabilizing the electrolyte, this material is favorable for the stability in a long-time usage, and the electric conductivity is also good. However, according to the review of this inventor, the oxidation resistance after using for a long time was not sufficient. The purpose of the present invention is to provide an inexpensive metallic separator material that forms an oxide film with good electric conductivity in the vicinity of 1,000°C, has good oxidation

resistance, and has a small thermal expansion difference from an electrolyte.

[0009]

(Means to solve the problems)

As a result of various reviews of this inventor, first, a ferrite system was adopted as a metallic material being used. Its first reason is that the thermal expansion coefficient from normal temperature to 1,000°C of the stabilized zirconia as an electrolyte is 11-12 x 10^{-6}/°C, whereas it is 16 x 10^{-6}/°C or higher in an ordinary austenite system metal. Since the thermal expansion difference of both of them is large, there is a problem in the stability during the long-time use. Its second reason is that the ferrite system has Fe as a base and does not include Ni or includes it at a small amount, though the austenite system is generally expensive since an expensive Ni is included.

[0010] Next, this inventor variously reviewed the electric conductivity of the oxide film being formed. As a representative oxide film having a protection, Al oxide and Cr oxide were reviewed. At high temperature in the vicinity of 1,000°C, the protective action is larger and more favorable in Al_2O_3. However, when the electric resistance of a material for forming the Al_2O_3 film was measured, it exceeded 100 mΩ·cm^2, and

it was understood that it could not be used as a separator. On the other hand, the electric resistance of a material for forming the Cr_2O_3 film was 100 $m\Omega \cdot cm^2$ or less, and it was understood that it could be used as a separator. Accordingly, in the present invention, a ferrite system metallic material for forming an oxide film mainly composed of a Cr system oxide on the surface, that is, a Fe-Cr system was adopted as a base.

[0011] Next, the problem in a long-time use is an oxidation resistance, and as mentioned above, at about 1,000°C, the oxidation resistance of an ordinary Cr system oxide film is inferior to that of an Al system film. Also, even if the Cr system oxide is used as a base, a Fe-base alloy (for example, Fe-Cr alloy such as SUS 430) is inferior to a Ni-base alloy (for example, Ni-Cr alloy represented by JIS NCF600). Therefore, it is difficult to meet the oxidation resistance simply by the Fe-Cr system.

[0012] This inventor variously reviewed the above-mentioned problems to solve them, and as a result, it was discovered that if Hf was added to the Fe-Cr system, a good oxidation resistance was obtained while having a Cr system oxide film as a main component and peeling-off of the film was not seen, even after heating for a long time. Also, it was discovered that if one kind or two kinds or more of Y, rare-earth elements, and Zr were

added, the oxidation resistance was further improved. Also, it was discovered that since the oxide film being formed by adding them was mainly composed of a Cr system oxide film, the electric resistance was not considerably large.

[0013] In other words, the present invention is a steel for a solid electrolyte type fuel cell separator comprised of 0.2% or less C, 3.0% or less Si, 1.0% or less Mn, 15-30% Cr, 0.5% or less Hf, and the balance substantial Fe by weight %. In the present invention, one kind or two kinds or more of 2% or less Ni, 1% or less Al, 1% or less Ti, 5% or less Mo + 1/2W of one kind or two kinds of Mo and W, and 2% or less Nb can be included.

[0014] Also, in the present invention, one kind or two kinds or more of 0.5% or less Y, 0.2% or less rare-earth elements, and 1% or less Zr is preferably included. More appropriately, the present invention is a steel for a solid electrolyte type fuel cell separator comprised of 0.08% or less C, 0.2-2.0% Si, 0.2-1.0% Mn, 18-25% Cr, 0.01-0.3% Hf, 0.9% or less Ni, 0.5% or less Al, one kind or two kinds or more of 0.01-0.3% Y, 0.01-0.12% rare-earth elements, and 0.05-0.8% or less Zr, and the balance substantial Fe by weight %.

[0015]

(Embodiment of the invention)

Next, the reasons for limiting the components in the present invention are mentioned. C has an action that increases the high-temperature strength by forming a carbide, however it degrades the workability and reduces an effective amount of Cr for the oxidation resistance by combining with Cr. Therefore, its amount is limited to 0.2% or less. Preferably, its amount is 0.08% or less. Si has an action that improves the oxide resistance by forming a thin SiO_2 system film in the vicinity of the interface of the Cr_2O_3 system oxide film and the base metal in the present invention. However, its excessive addition lowers the workability and the toughness, the SiO_2 system film is too thick, and the electric conductivity of the film is lowered. Thus, its amount is set to 3% or less. Preferably, its amount is 0.2-2.0%.

[0016] Mn is required to improve the adhesion of the Cr_2O_3 system oxide film. However, if it is excessively added, the oxide resistance is deteriorated due to the shortage of the oxidation resistance of a spinel type oxide containing Mn. Therefore, Mn is limited to 1% or less. Preferably, its amount is 0.2-1.0%. Cr is an important element for maintaining the oxidation resistance and the electric conductivity by the generation of the Cr_2O_3 system oxide film in the present invention. For this reason, at least 15% is required. However, if it is excessively

added, not only there is no considerable effect on the oxidation resistance improvement, but the workability is degraded. Thus, its amount is limited to 15-30%. Preferably, its amount is 18-25%. Hf is an important element in the present invention. As mentioned above, it is difficult to render good oxidation resistance by only the Cr system oxide film, however it was found out that the oxidation resistance was largely /4 improved by adding a small amount of Hf. It is considered that it is mainly due to the improvement effect of the adhesion of the oxide film. However, since its excessive addition degrades the hot-workability, its amount is limited to 0.5% or less. Preferably, its amount is 0.01-0.3%.

[0017] Y, rare-earth elements, and Zr have an effect that further improves the oxidation resistance by adding it at a small amount in combination with Hf. However, since its excessive addition degrades the hot-workability, Y is limited to 0.5% or less, the rare-earth elements are limited to 0.2% or less, and Zr is limited to 1% or less. Preferably, Y is 0.01-0.3%, the rare-earth elements are 0.01-0.12%, and Zr is 0.05-0.8%. Also, if Hf and one kind or two kinds or more of Y, rare-earth elements, and Zr are combined with an appropriate amount of Si and Mn, the oxidation resistance is further improved. It is considered that it is mainly due to the adhesion improvement

of the oxide film by the compounding action of these elements. Also, Zr forms a carbide by combining with C similarly to Ti and Nb which will be mentioned later, improves the workability by fixing C, and also contributes to the strength improvement.

[0018] Each element of Ni, Al, Ti, Nb, To, and W is not necessarily required to be added to the steel of the present invention, however since they have the following effects, they can be added alone or by mixing, if necessary. Ni is effective for the improvement of the toughness by adding a small amount to the steel of the present invention. However, Ni is an element for generating an austenite, and its excessive addition is a two-phase structure of ferrite-austenite, so that the thermal expansion coefficient is increased, and the cost is raised. Furthermore, an excessive addition of Ni deteriorates the oxidation resistance. Therefore, Ni is limited to 2% or less. Preferably, its amount is 0.9% or less.

[0019] Al is added as a deoxidizer. If Al is added at a large amount, an Al_2O_3 film is formed, however as mentioned above, though the Al_2O_3 film is effective for the oxidation resistance, it increases the electric resistance of the oxide film. Therefore, in the present invention, Al is limited to 1% or less to avoid the formation of the Al_2O_3 film. Preferably, its amount is 0.5% or less. Ti forms a carbide by combining with C and

improves the workability by fixing C. However, it forms TiO or TiO_2 having no considerable protection in the vicinity of 1,000°C and degrades the oxidation resistance. Therefore, Ti is limited to 1% or less. Nb forms a carbide by combining with C similarly to Ti, improves the workability by fixing C, and also increases the high-temperature strength. However, since its excessive addition degrades the oxidation resistance, its amount is limited to 2% or less.

[0020] Since Mo and W have an action that increases the high-temperature strength in particular, it may be added if the high-temperature strength is considered important. However, if it is excessively added, since the oxidation resistance and the workability are degraded, it is limited to 5% or less as Mo + 1/2W. With the above-mentioned alloy composition, preferably, a steel for a solid electrolyte fuel cell separator in which the electric resistance of an oxide film at 1,000°C after heating at 1,000°C for 100 h is 50 $m\Omega\cdot cm^2$ or less and peeling-off of the surface oxide scale is not substantially caused after heating at 1,100°C for 100 h can be obtained.

[0021] Also, the following elements can be added in a range where the electric resistivity of an oxide film at 1,000°C after heating at 1,000°C for 100 h is 80 $m\Omega\cdot cm^2$ or less and t4he scale peeling-off after heating at 1,100°C for 100 h meets 0.5 mg/cm^2

or less can be included. For example, additive elements in the following ranges can be included.

P ≤ 0.04%, S ≤ 0.03%, Cu ≤ 0.30%, V ≤ 0.5%, Ta ≤ 0.5%, Mg ≤ 0.02%, Ca ≤ 0.02%, and Co ≤ 2%.

[0022]

(Application examples)

Application Example 1

10 kg ingot was prepared by melting a steel with a composition shown in Table 1 by a vacuum induction furnace, heated to 1,100°C, and forged and elongated to a bar material of 30 mmØ. Also, in Table 1, a comparative steel No. 41 is an austenite system alloy known as NCF600. Also, a comparative steel No. 44 described in Japanese Kokai Patent Application No. Hei 6[1994]-264193. In the manufacturing processes of these samples, slight flaws were generated during forging in No. 9 alloy with a relatively high amount of Cr among the steels of the present invention, and the workability tended to be slightly poor. Specimens were cut out of these materials and subjected to various kinds of tests.

[0023]

(TABLE 1)

		C	Si	Mn	Ni	Cr	Al	Ti	Nb	Mo	W	Fe	Hf	Y	希土類元素	Zr
本発明鋼	1	0.02	0.35	0.51	0.22	22.54	0.26	–	–	–	–	Bal	0.03	–	–	–
	2	0.02	0.33	0.50	0.24	22.23	0.22	–	–	–	–	Bal	0.09	–	La0.04	–
	3	0.03	0.45	0.63	0.12	24.10	0.12	0.21	–	–	–	Bal	0.15	0.02	–	–
	4	0.02	0.44	0.65	0.25	20.34	0.21	–	–	–	–	Bal	0.05	–	–	0.22
	5	0.03	0.46	0.55	0.20	20.12	0.25	–	–	–	–	Bal	0.02	–	Ce 0.02	0.25
	6	0.02	0.47	0.54	0.24	24.08	0.23	0.25	–	–	–	Bal	0.04	0.02	La 0.02	0.15
	7	0.12	0.35	0.53	0.24	22.05	0.24	–	–	–	–	Bal	0.09	–	–	–
	8	0.03	0.46	0.47	0.35	16.10	0.22	–	–	–	–	Bal	0.34	–	–	–
	9	0.02	0.41	0.38	0.36	28.31	0.26	–	–	–	–	Bal	0.04	–	–	–
	10	0.02	0.40	0.45	0.54	19.24	–	0.84	1.2	–	–	Bal	0.11	0.03	La 0.02, Ce 0.01	–
	11	0.06	0.45	0.44	1.55	21.04	0.25	–	–	2.53	–	Bal	0.08	–	–	–
	12	0.03	2.51	0.56	0.24	20.35	–	–	–	–	3.7	Bal	0.02	–	La 0.04	–
	13	0.03	0.55	0.55	0.54	20.10	0.23	–	0.54	1.5	2.3	Bal	0.04	–	La 0.04	0.14
	14	0.02	0.50	0.84	–	22.35	0.34	0.24	–	–	–	Bal	0.09	–	–	–
	15	0.02	0.52	0.41	–	22.12	–	0.31	–	–	–	Bal	0.07	–	La 0.03	0.24
	16	0.03	0.10	0.55	0.11	22.18	–	0.14	–	–	–	Bal	0.05	–	La 0.04	–
	17	0.04	0.46	0.11	0.14	22.49	0.31	–	–	–	–	Bal	0.06	–	La 0.04	–
	18	0.02	0.11	0.08	0.15	20.18	0.24	–	–	–	–	Bal	0.07	–	La 0.03	–
	19	0.03	0.47	0.52	0.25	23.33	0.75	0.05	–	–	–	Bal	0.06	–	Ce 0.01	–
比較鋼	41	0.03	0.22	0.41	Bal	18.22	0.20	0.33	–	–	–	8.72	–	–	–	–
	42	0.06	0.49	0.62	0.20	19.75	2.53	1.22	–	–	–	Bal	–	–	–	–
	43	0.02	0.29	0.12	0.26	24.39	4.06	–	–	–	–	Bal	–	–	–	–
	44	0.03	1.02	0.53	23.50	21.35	3.50	–	–	–	–	Bal	–	–	–	–
	45	0.04	0.44	0.65	0.21	10.25	0.21	0.10	–	–	–	Bal	0.04	–	–	–
	46	0.04	0.45	0.43	0.21	22.05	0.10	0.21	–	–	–	Bal	–	–	–	–
	47	0.03	0.12	0.43	0.10	21.30	0.15	0.12	–	–	–	Bal	–	–	La 0.03	–
	48	0.04	3.42	0.36	0.23	19.80	0.21	0.20	–	–	–	Bal	–	–	La 0.02	–
	49	0.03	0.44	0.02	0.21	22.52	0.23	0.20	–	–	–	Bal	–	–	La 0.02	–
	50	0.03	0.38	1.35	0.21	33.04	0.34	0.19	–	–	–	Bal	–	–	La 0.03	–

/5

1. Rare-earth elements

2. Steel of the present invention

3. Comparative steel

[0024] First, a columnar specimen with a diameter of 10 mm and a length of 20 mm was heat-treated at 1,000°C for 100 h in the air, and the kind of oxide being generated on the surface was investigated by an X-ray diffraction. Furthermore, the amount of surface oxide scale being peeled off was measured. Also, a plate-shaped sample of 10 mm x 10 mm x 3 mm was heated at 1,000°C

for 100 h in the air, an oxide film was formed on the surface, and the electric resistance at 1,000°C was measured. Also, the electric resistance was shown by an area resistance (mΩ·cm^2). Also, in almost all the samples, since peeling-off of the oxide scale was not seen after heating 1,000oC for 100 h, the amount of oxide scale being peeled off after heating at 1,100oC for 100 h and at 1,000°C for 1,000 h was investigated as an acceleration test. Furthermore, for several samples, the thermal expansion coefficient from 30°C to 1,000°C was measured. These test results are summarized in Table 2.

[0025]

(TABLE 2)

/6

		熱膨張係数 30〜1000℃ (×10⁻⁶/℃)	1000℃×100Hr加熱後			1100℃×100Hr加熱後	1000℃×1000Hr加熱後
			生成酸化物	スケール剥離量 (mg/cm²)	1000℃における電気抵抗 (mΩ·cm²)	スケール剥離量 (mg/cm²)	スケール剥離量 (mg/cm²)
本発明鋼	1	12.6	Cr_2O_3, $MnFe_2O_4$	0.00	12	0.00	0.18
	2	13.0	Cr_2O_3, $MnFe_2O_4$	0.00	18	0.00	0.00
	3	13.1	Cr_2O_3, $MnFe_2O_4$, TiO_2	0.00	20	0.00	0.00
	4	12.8	Cr_2O_3, $MnFe_2O_4$	0.00	22	0.00	0.05
	5	12.8	Cr_2O_3, $MnFe_2O_4$	0.00	26	0.00	0.00
	6	未測定	Cr_2O_3, $MnFe_2O_4$, TiO_2	0.00	10	0.00	0.00
	7	未測定	Cr_2O_3, $MnFe_2O_4$	0.00	43	0.00	0.52
	8	未測定	Cr_2O_3, $MnFe_2O_4$	0.00	30	0.00	0.82
	9	未測定	Cr_2O_3, $MnFe_2O_4$	0.00	42	0.00	0.21
	10	未測定	Cr_2O_3, $MnFe_2O_4$, TiO_2	0.00	25	0.00	0.85
	11	未測定	Cr_2O_3, $MnFe_2O_4$	0.00	20	0.00	0.33
	12	未測定	Cr_2O_3, $MnFe_2O_4$	0.00	62	0.00	0.29
	13	未測定	Cr_2O_3, $MnFe_2O_4$	0.00	18	0.00	0.25
	14	未測定	Cr_2O_3, $MnFe_2O_4$, TiO_2	0.00	31	0.00	0.25
	15	未測定	Cr_2O_3, $MnFe_2O_4$, TiO_2	0.00	15	0.00	0.00
	16	未測定	Cr_2O_3, $MnFe_2O_4$	0.00	32	0.12	0.54
	17	未測定	Cr_2O_3, $MnFe_2O_4$, TiO_2	0.00	30	0.15	0.68
	18	未測定	Cr_2O_3, $MnFe_2O_4$, TiO_2	0.00	19	0.22	0.79
	19	未測定	Cr_2O_3, $MnFe_2O_4$	0.00	58	0.00	0.90
比較鋼	41	16.7	Cr_2O_3, $MnFe_2O_4$	0.00	10	0.91	0.18
	42	14.2	Al_2O_3, TiO_2	0.00	380	0.00	未測定
	43	14.5	Al_2O_3	0.00	452	0.00	未測定
	44	17.3	Al_2O_3, Cr_2O_3	0.00	153	0.00	未測定
	45	13.3	Cr_2O_3, $MnFe_2O_4$, TiO_2	4.50	61	5.30	未測定
	46	13.0	Cr_2O_3, $MnFe_2O_4$, TiO_2	0.00	28	1.92	未測定
	47	未測定	Cr_2O_3, $MnFe_2O_4$, TiO_2	0.00	42	1.47	未測定
	48	未測定	Cr_2O_3, $MnFe_2O_4$, TiO_2	0.00	109	0.00	未測定
	49	未測定	Cr_2O_3, TiO_2	0.00	26	2.70	未測定
	50	未測定	Cr_2O_3, $MnFe_2O_4$, TiO_2	0.53	55	1.90	未測定

1. Thermal expansion coefficient, 30-1,000°C (x 10^{-6}/°C)

2. After heating at 1,000°C for 100 h

3. After heating at 1,100°C for 100 h

4. After heating at 1,000°C for 1,000 h

5. Oxide generated

6. Amount of scale peeled off (mg/cm^2)

7. Electric resistance at 1,000°C (mΩ·cm^2)

8. Steel of the present invention

9. Comparative steel

10. Unmeasured

[0026] From Table 2, in the steels of the present invention, a Cr_2O_3 film is mainly formed by heating at 1,000°C for 100 h in the air, and the electric resistance value is sufficiently small. On the other hand, in comparative steel Nos. 42, 43, and 44, since Al is included at 2% or more, an Al_2O_3 film is formed, and the electric resistance value is much larger than the value of the steels of the present invention. Also, in a comparative steel No. 48, since Si is high, it is considered that a SiO_2 system film is probably formed, though it could not be confirmed by an the X-ray diffraction from the surface, and the electric resistance value is high. Compared with the amount of surface scale being peeled off after heating at 1,000°C for 100 h in the air, in the steels of the present invention, no peeling-off of the scale was observed, since the amount of Cr is small in a Comparative steel No. 45, it can be understood that it cannot withstand a long-time use. Also, in a comparative steel No. 50, peeling-off of the scale was observed, and it is considered that

Mn is high and the amount of Mn_2FeO_4 is increased in addition to no Hf content.

[0027] Furthermore, in the comparison of the amount of surface scale being peeled off after heating at 1,100°C for 100 h in the air as an acceleration test, peeling-off of the scale is not observed in the steels of the present invention except for Nos. 16, 17, and 18, even by heating at high temperature of 1,100°C. In Nos. 16, 17, and 18, though peeling-off of a very small amount of scale is observed, the reason for this is considered that the amount of Mn is low. On the other hand, in comparative steel Nos. 41 (NCF600), 45, 46, 47, 49, and 50, peeling-off was caused. The reason for this is considered that the adhesion of the scale is deficient since Hf, Y, rare-earth elements, Zr are not added in No. 46; Hf is not included and the amount of Si is low in No. 47; and Hf is not included and the amount of Mn is low in No. 49. The reason for this is considered that in No. 50, as mentioned above, Hf is not included and Mn is too high.

[0028] In the comparison of the amount of surface scale being peeled off after heating at 1,000°C for 1,000 h in the air as another acceleration test condition, it is understood that the amount of scale being peeled off is slightly large in the steels of the present invention because of high C (No. 7), low Cr (No. 8), high Nb and Ti (No. 10), low Si (No. 16), low Mn (No. 17),

and low Si and Mn (No. 18). Then, the thermal expansion coefficient value from normal temperature to 1,000°C is about 13 x 10^{-6}/°C in steel Nos. 1-5 of the present invention and is close to the zirconia value. On the other hand, in comparative steels Nos. 41 and 44, the thermal expansion coefficient is large since it is an austenite system.

[0029]

(Effects of the invention)

As mentioned above, with the use of the steel of the present invention in a separator of a solid electrolyte type fuel cell, the cost of the fuel cell can be reduced, so that the steel of the present invention can largely contribute to the practicality and the large scale of the fuel cell.